Hydrolysis of N_2O_5 and $C10N0_2$ on the $H_2SO_4/HNO_3/H_2O$ Ternary Solutions under Stratospheric Conditions

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ABSTRACT

The reaction probabilities of N_2O_5 and $C10N0_2$ with H_2O on liquid sulfuric acid surfaces have been reexamined to survey the effect of HNO_3 on these two hydrolysis rates, using a fast flow reactor coupled to a chemical ionization mass spectrometer. The measurements were carried out by maintaining constant H_20 and HNO_3 partial pressures and by varying temperatures between 227 and 195 K in order to mimic compositions representat ive of stratospheric aerosols. For experiments excluding HNO_3, the reaction probability of N_2O_5 hydrolysis was found to be near 0.1, independent of temperature and H_2SO_4 content, This is in agreement with results previously measured under similar conditions. In the presence of gaseous HNO_3 at stratospheric concentrations, the reaction probability y was observed to decrease from about 0.09 at 218 K to about 0.02-0.03 at 195 K for P_{H2O} = 3.8x104- 1.Ox 10^{-3} Torr, showing that incorporation of HNO_3 into liquid sulfuric acid greatly retarded the N_2O_5 hydrolysis. The $ClONO_2$ reaction with H_2O on liquid sulfuric acid, on the other hand, did not appear to be affected by the presence of HNO_3.

(Submitted to GRL, Dec. 15, 1994)

INTRODUCTION

The impact of heterogeneous reactions occurring on sulfate aerosols on stratospheric chemistry is now well recognized. One of these important reactions involves deactivation of oxides of nitrogen (NO_x) via reaction of N_2O_5 with H_2O on liquid sulfate aerosols,

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{1}$$

In the stratosphere, the fate of NO_x is governed by the. photochemical dissociation of N_2O_5 and reactions with ClO and OH radicals. Hence reaction (1) will reduce stratospheric NO_2 concentrations and, consequently, result in increasing abundances of ClO and OH, leading to catalytic ozone depletion. Recent model calculations have indicated that reaction (1) may account for a significant fraction of the larger-than-expected ozone trend outside of the polar regions [e.g., Rodriguez et al., 1991]. $ClONO_2$ hydrolysis on liquid sulfate aerosols,

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \tag{2}$$

has also been proposed to play a role in direct chlorine activation at high latitudes in winter and early spring [e.g., Kolb et al., 1994].

Early laboratory studies [Mozurkewich and Calvert, 1988; Hanson and Ravishankara, 1991; Van Doren et al., 1991; Williams et al., 1994] revealed that the reaction probability of N_2O_5 hydrolysis is independent of temperature, sulfuric acid content, and even aerosol particle size, with a value of about 0.1. These results have been recently confirmed by measurements using submicron aerosol particles [Fried et al., 1994; Hanson and Lovejoy, 1994]. In contrast, $ClONO_2$ hydrolysis has been shown to depend strongly on sulfuric acid content [e.g., Kolb et al., 1994]. In the lower stratosphere, gas-phase HNO_3 exists at concentrations of a few ppbv and is in active equilibrium with sulfate aerosols. Furthermore, at colder temperatures typical of high latitudes in winter and early spring, a $H_2SO_4/HNO_3/H_2O$ ternary system has been suggested to form prior to the onset of PSCs [Zhang et al., 1993]. Thus, laboratory measurements are necessary to investigate the effect of the presence of HNO_3 in liquid sulfuric acid on the reaction probabilities for (1) and (2).

In this paper we present laboratory experiments designed specifically to answer this question. By maintaining constant H_2O and HNO_3 partial pressures and varying temperature, we are able to perform reaction probability measurements on acid surfaces with compositions representative of stratospheric aerosols. In a separate publication, we have reported results of uptake coefficients for the $ClONO_2$ and HOCl reactions with HCl on the $H_2SO_4/HNO_3/H_2O$ ternary system [Zhang et al., 1994a].

Experimental

Measurements of uptake coefficients were performed in a horizontally mounted flow reactor in conjunction with chemical ionization mass spectrometry (CIMS) detection. Detailed description of the experimental apparatus and procedures has been given elsewhere [Leu et al., 1994; Zhang et al., 1994a; Zhang et al., 1994b], and only a brief overview is presented here along with features pertinent to this work.

Liquid sulfuric acid films were prepared by totally wetting the inside walls of the flow reactor with acid solutions. Two approaches were used to simulate stratospheric aerosol compositions. In the first, the inside wall of the flow reactor was coated with a liquid sulfuric acid film about 75 wt %, and the film was then exposed to H_2O and HNO_3 by allowing the vapors to equilibrate with the liquid. As suggested previously [Zhang et al., 1993], the volubility of HNO_3 in sulfuric acid increases dramatically with decreasing temperature at constant H_2O and HNO_3 partial pressures. Hence, at low temperatures (< 200 K), the liquid film consisted virtually of a $H_2SO_4/HNO_3/H_2O$ ternary solution. The compositional change of the liquid surface in the flow tube resembled that of a droplet in the stratosphere: a decrease in temperature lowered both H_2O and HNO_3 vapor pressures and equilibrium was re-established by a change in the acid content through co-condensation of H_2O and HNO_3. Additional y, measurements were conducted directly on the liquid $H_2SO_4/HNO_3/H_2O$ ternary solutions prepared by mixing concentrated H_2SO_4 (~ 96 wt %) and HNO_3 (- 70 wt %) solutions with distilled water, to form compositions equivalent to those predicted for stratospheric aerosols at low temperatures.

Reactants and products were selectively detected using the CIMS. The 1^- ions, initiated by electron attachment to CF_3I, were used to detect N_2O_5 and $ClONO_2$ in the presence of HNO_3 since 1^- reacts readily with N_2O_5 and $C10N0_2$ to produce NO_3^- (62 amu), but not with HNO_3. At higher HNO_3 concentrations, the reaction of HNO_3 with 1^- also contributed to NO_3^-. In this case, the signal derived from HNO_3 reaction with 1^- was subtracted from that due to N_2O_5 or $ClONO_2$

when deducing the first-order loss rate coefficient. Higher HNO_3 concentrations also led to a substantial I" loss as a result of I^- attachment to HNO_3 ($HNO_3 \cdot I^-$, 190 amu). Alternatively, SF_6^- was used to monitor $ClONO_2$ as $NO_3^- \cdot FCl$ (116 amu) or $ClONO_2^-$ (97 amu), but an excess of HNO_3 almost completely converted SF_6^- into $NO_3^- \cdot HNO_3$ (125 amu) and NO~-02HNO~(188 amu). The fluoride ions, F^-, were employed to detect HOC1 and HCl corresponding to ClO^- (51 amu) and Cl^- (35 amu), respectively. Partial pressures of the reactant species (N_2O_5 and $ClONO_2$) in the neutral flow tube were maintained at about 5.0x 10"7 Torr, characteristic of the stratosphere. These low concentrations were also essential to minimize the occurrence of secondary reactions of the product ions.

H_2O was admitted to the flow tube with the main He carrier gas. The partial pressure of H_2O was estimated by passing a known flow of He carrier gas through a H_2O reservoir at room temperature. It was controlled by diluting the humidified He flow (assuming 100% RH) with a dry He flow. In addition, we measured $ClONO_2$ hydrolysis on a liquid H_2SO_4/H_2O film and obtained its composition, on the basis of our earlier data of reaction probabilities for this binary system [Zhang et al., 1994a], to verify the above method. The estimated uncertainty in determination of the H_2O partial pressure was about ±25 %. HNO_3 was delivered through a jacketed sliding injector by circulating a room temperature solution of ethylene glycol in water.

The flow tube was operated at a pressure of about 0.40 Torr, with the average carrier gas flow velocity ranging from 1500 to 1900 cm s-'. Reaction probabilities (γs) were calculated using the standard cylindrical flow tube analysis [Brown, 1978].

Results and Discussion

N_2O_5 Hydrolysis Figure 1 illustrates the loss of N_2O_5 as a function of injector position as N_2O_5 was exposed to three different acid solutions. The solid circles correspond to an experiment on a ternary solution containing 41 wt% HNO_3 and 5 wt % H_2SO_4 at 220 K. The open squares refer to a measurement at 195 K with H_2O and HNO_3 at partial pressures of 3.8x10< and 5.0x 10-7 Torr, respect ivel y; the acid content was estimated to be 16.4 wt% HNO_3 and 29.4 wt% H_2SO_4. The data without HNO_3 are plotted as open triangles for an experiment performed at 200 K and P_{H2O} = 3.8x104 Torr, with an estimated sulfuric acid content of 53 wt %. These measurements were

conducted at a partial pressure of N_2O_5 of - 5.0x 10^{-7} Torr. Reaction probabilities were calculated from the pseudo-first-order coefficient corresponding to the N_2O_5 decay, derived from the linear least-squares analysis of plots of log $[N_2O_5]$ vs injector distance. It is apparent in the figure that the loss of N_2O_5, and hence the uptake coefficients, decrease as the amount of HNO_3 in the solution increases. The y value reaches a minimum for the ternary solution containing 41 wt % HNO_3 and 5 wt % H_2SO_4, an extreme case predicted for stratospheric aerosols at 191 K for 5 ppmv H_2O and 10 ppbv HNO_3 at 100 mb (corresponding to an shit ude of - 16 km) assuming that nucleation of polar stratospheric clouds (PSCs) has been inhibited [Carslaw et al., 1994]. Note that the temperature at which this measurement was carried out was about 30 degrees higher than that expected in the polar stratosphere, due to higher freezing points of the HNO_3-rich ternary solutions in the flow tube. As discussed below, the N_2O_5 hydrolysis indeed shows little dependence on temperature in the range of 195 to 230 K.

The N_2O_5 hydrolysis was studied as a function of temperature while holding both H_20 and HNO_3 pressures constant. In these experiments, it was important to ensure an equilibrium between the liquid and gas phases. For HNO_3, this can be verified by pulling the injector upstream while monitoring its recovery using the CIMS. The N_2O_5 uptake coefficient data are shown in Figure 2 as a plot of y versus temperature over the range of 195-230 K. In Figure 2(a), the measured reaction probabilities on HNO_3-free sulfuric acid surfaces are nearly independent of temperat ure (i.e. H_2SO_4 wt %), with a value close to 0.1. Each y in this figure was determined by calculating the average of at least four measurements. The solid line is a linear fit through the data. A H_2O partial pressure of 3.8x10^4 Torr was used in this experiment. In general, our measured reaction probabilities on liquid sulfuric acid surfaces free of HNO_3 are in close agreement with the results previously reported in the literature [e.g., Mozurkewich and Calvert, 1988; Hanson and Ravishankara, 1991; Van Doren et al., 1991].

Figures 2 (b) and (c) show the measurements in the presence of HNO_3 at a partial pressure of - 5,0x 10"^{7} Torr, conducted at H_2O partial pressures of 1.0x10^{-3} and 3.8x10^4 Torr, respectively. It is clear in the figure that y varies with temperature, a change in temperature from 195 to218 K results in y values from 0.03 to 0.09 for P_{H2O} = 3.8x10^4 Torr (a linear least squares fit of y versus temperature yields an expression of γ = -0.386 + 0.00212 *Tin* the temperature range of 195 to 220 K for (c)). This occurs because of increasing HNO_3 dissolution in sulfuric acid at low temperatures: volubility of HNO_3 in sulfuric acid increases as H_2SO_4 content and temperature decrease [Zhang et al., 1993], For the H_2O and HNO_3 vapor pressures of **3.8x104** and 5.0x 10-7 Torr, for example, the content of the liquid film was estimated to vary from about 75 wt % sulfuric acid with a residual amount of HNO_3 (< 0.1 wt %) to about 30 wt % H_2S0_4 and 15 wt % HNO_3 [Molina et al., 1993; Zhang et al., 1993; Beyer et al., 1994; Tabazadeh et al., 1994; Carslaw et al., 1994], when the temperature was regulated from 230 to 195 K. Moreover, as depicted in this figure, at low temperatures (< 200 K) the uptake coefficients in Figure 2(c) (i.e. with a lower H_2O partial pressure) slightly exceeds that in Figure 2(b). The lowest y attained at 195 K in Figure 2(b) is consistent with that observed for the ternary solution of 41 wt % HNO_3 and 5 wt % H_2SO_4 shown in Figure. 1. As mentioned above, such a solution represents the highest HNO_3 content which could dissolve in the stratospheric aerosols under normal stratospheric conditions. Hence, the value of 0.02 is likely to be interpreted as the lower limit for the N_2O_5 hydrolysis on liquid aerosols in the stratosphere.

The results displayed in Figure 2 are also tabulated in Table I, along with the estimated acid composition for each measurement. In addition, measurements were carried out on two ternary solutions (41 wt % HNO_3, 5 wt % H_2SO_4 and 10 wt % HNO_3, 40 wt % H_2SO_4) prepared by mixing appropriate concentrated acids. Also listed in Table I for comparison is one set of measurements performed on a partially frozen ternary solution with 41 wt % HNO_3 and 5 wt % H_2SO_4; the resulting reaction probability is about 0.01. This value is larger than that measured on nitric acid contaminated ice surfaces [Hanson and Ravishankara, 1991] and sulfuric acid hydrates [e.g., Zhang et al., 1994b]. In fact, this case likely corresponds to a partially frozen surface with nitric acid trihydrate (NAT) and liquid sulfuric acid coexisting, as indicated by the fact that the N_2O_5 uptake coefficient measured after evaporation of the solid constituent was comparable to that measured on a liquid sulfuric acid surface (evaporation of a NAT film was very rapid at 220 K). Partially frozen mixtures of the $H_2SO_4/HNO_3/H_2O$ ternary solutions were previously observed using FTIR [Iraci et al., 1994] and thermal analysis techniques [Beyer et al., 1994]. These results also showed that sulfuric acid hydrates only form subject to subsequent warming (after the initial freezing).

As shown in Figure 1, the uptake coefficient of N_2O_5 hydrolysis on the HNO_3-rich ternary solution is about a factor of 5 smaller than that on a sulfuric acid surface free of HNO_3. The reduced react ivit y with increasing H NO_3 appears to reflect the nature of the reaction mechanism, which was suggested to be limited by an ionic equilibrium [Mozurkewich and Calvert, 1988],

$$N_2O_5\ (aq) \leftrightarrow NO_2^+(aq) + NO_3^-\ (aq) \tag{3}$$

HNO_3 dissolved in sulfuric acid also dissociates to yield NO_3^- [Zhang et al., 1993], thus potentially suppressing the dissociation of N_2O_5 and resulting in a lower volubility of N_2O_5 in the $H_2SO_4/HNO_3/H_2O$ ternary solution. In addition, reaction (1) has been suggested to occur primarily on the surface, independent of the aerosol size [Hanson and Love joy, 1994].

It is widely believed that in the global stratosphere the observed abundances of nitrogen and chlorine species can not be accurately simulated in numerical models by gas phase processes alone, but that inclusion of N_2O_5 hydrolysis on sulfate aerosols (with y ≈ 0.1) produces better agreement bet ween observations and calculations [e.g., Rodriguez et al., 1991]. Recent studies, however, cast some doubt about the magnitude of this reaction probability [Fahey et al., 1993; Fan and Wofsy, 1994, private communication]; a value of 0.1 used in the numerical models tends to underest imate the stratospheric NO_x/NO_y ratio. As demonstrated in the present work, this could occur if a significant amount of HNO_3 incorporates into the stratospheric aerosols. Alternatively, the N_2O_5 hydrolysis could be reduced if the aerosols are partially or completely frozen [e.g., Zhang et al., 1994b]. In the most recent study of Hanson and Lovejoy [1994], it was also proposed that the observed decrease in the reaction probability of N_2O_5 hydrolysis on 60 wt % submicron-sized liquid sulfuric acid aerosols may be attributable to the presence of HNO_3 [Fried et al., 1994].

Lastly, attention was paid to the possibility of N_2O_5 reaction with HC1 in sulfuric acid as well as in the $H_2SO_4/HNO_3/H_2O$ ternary solution at low temperatures (< 200 K). Our earlier results indicate that the reactions between $C10N0_2$ and HOCl with HCl proceed extremely efficiently when the temperature is below 200 K, because of increasing amounts of HCl dissolved in the liquid [Zhang et al., 1994a]. With HC1 partial pressures in the range of 10^{-6} to 10^{-7} Torr, there was no observable enhancement in the uptake. coefficient over the corresponding N_2O_5 hydrolysis value. This implies that direct reaction between N_2O_5 and HCl on liquid stratospheric aerosols may be of less importance, even at low temperatures.

$ClONO_2$ Hydrolysis. $C10N0_2$ hydrolysis on $H_2SO_4/HNO_3/H_2O$ ternary solutions was investigated in the same manner as the N_20_5 hydrolysis. Figure 3 is the same as Figure 1 except for $ClONO_2$

reaction with H_2O on three different solutions: 41 wt % $HN0_3$ and 5 wt % H_2SO_4 at 220 K (solid circles) and with (open squares) and without (open triangles) $HN0_3$ at 196 K and P_{H2O} = 3.8x104 Torr. The corresponding reaction probabilities for these solutions are 0.051, 0.039, and 0.041, respectively. As shown in this figure, the difference of $C10N0_2$ hydrolysis in the latter two cases is negligible within the experimental precision, showing that the presence of $HN0_3$ in sulfuric acid has no noticeable impact on the $ClONO_2$ hydrolysis. The slightl y higher γ value for the HNO_3-rich ternary solution may be explained by its higher H_20 content (or H_20 activity).

Figure 4 presents the reaction probability of $C10N0_2$ with H_20 as a function of temperature at P_{H2O} = 3.8x104 Torr and P_{HNO3} = 5.0x 10^{-7} Torr (open circles). Also shown as the solid curve is the reaction probability measured previously by us on the H_2SO_4/H_2O binary solution under ident ical experimental conditions [Zhang et al., 1994a]. Clearly, the y measured on the ternary solutions did not change appreciably from that on the binary solutions. This implies that the $ClONO_2$ hydrolysis on stratospheric aerosols is dependent only on the H_20 act ivit y, increasing when the stratospheric dew point temperature is approached (the dew point temperature is about 186 K for a 5 ppmv H_2O mixing ratio at 100 rob). Analogous to this observation are the reactions involving $C10N0_2$ and HOCl with HCl reported by us previously [Zhang et al., 1994a]: the reaction probabilities are determined primarily by the amount of dissolved HCl in sulfuric acid, which is also not affected by the dissolution of HNO_3.

Conclusions

In this paper we have presented laboratory measurements of N_2O_5 and $ClONO_2$ hydrolysis in order to examine the effect of HNO_3 dissolved in sulfuric acid on the reaction probabilities. The data reveal that the presence of HNO_3 in sulfuric acid in general reduces the N_2O_5 hydrolysis. At mid-latitudes, where the ambient temperatures in the lower stratospheric are higher than 210 K, the HNO_3 content in sulfate aerosols is minimal and this effect would be less important. At high latitudes in winter and early spring, the amount of $HN0_3$ in stratospheric aerosols increases with decreasing temperature. and, consequently, the reaction probability of N_2O_5 hydrolysis decreases with decreasing temperature. For a H_2O partial pressure of 3.8x104 Torr (equivalent to about a 5 ppmv H_20 mixing ratio at 100 mb in the stratosphere), the reaction probability decreases from 0.09 at 218 K to about 0.03 at 195 K. A lower limit for N_2O_5 hydrolysis on liquid stratospheric aerosols has been determined to be about 0.02. The $ClONO_2$ hydrolysis, however, is shown to be independent of the presence of HNO_3 in sulfuric acid. The results suggest that in the stratosphere, the $ClONO_2$ hydrolysis is only governed by the H_2O content of the acid solution, and is proportional to the H_2O activity.

Acknowledgements. This study has been motivated and greatly benefited by discussions with S. M. Fan and S. C. Wofsy of the Harvard University. We are also grateful to S. L. Clegg of University of East Anglia, UK and B. P. Luo of Max- Planck-Institut fur Chemie, Germany for providing programs to calculate stratospheric aerosol compositions. The research was performed at the Jet Propulsion Laboratory, California Institute Technology, under a contract with the National Aeronautics and Space Administration (NASA).

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Table 1. Summary of Measured Reaction Probabilities for N_2O_5 Hydrolysis*

Temperature (K)	P_{H2O} (Torr)	H_2SO_4 wt %[b]	HNO_3 wt %[b]	γ
227.1	3.8x10-4	*74.5*	0.0	0.099[c]
226.0	3.8x10-4	*73.7*	0.0	0.096'
225.0	3.8x10-4	*73.5*	0.0	0.097'
218.9	3.8X10 4	*70.2*	0.0	0.12'
215.0	3.8x10-4	*67.2*	0.0	0.11'
205.6	3.8x10-4	*60.2*	0.0	0.10[c]
197.6	3.8x10 4	51.1	0.0	0.10[c]
195.0	3.8x10 4	45.8	0.0	0.1 1[c]
218.0	3.8x10 <	*69.6*	< 0.1	0.089
215.8	3.8x10 4	*68.4*	< 0.1	0.082
214.0	3.8x10 4	*67.5*	< 0.1	0.070
210.0	3.8x10 4	64.6	< 0.1	0.075
210.0	3.8x10 4	64.6	< 0.1	0.068
203.3	3.8x10 4	57.8	*0.6*	0.059
201.6	3.8x10 4	54.1	*1.2*	0.065
201.6	3.8x10 4	54.1	1.2	0.042
199.1	3.8x10 4	49.0	2,4	0.047
196.0	3.8x10 4	37.4	9.7	0.039
195.0	3.8x10 4	29.4	16.4	0.034
214.7	1 .0x 10"3	*62.3*	< 0.1	0.084
214.7	1 .0x 10-3	*62.3*	< 0.1	0.073
210$1	1.0X10"3	*56.8*	0.2	0$088
206.8	1 .0x 10-3	*52.5*	0.5	0.055
205.4	1 .0x 10-3	*50.3*	0.9	0.055
200.9	1.Ox10-3	*35.8*	7.7	0.051
200.9	1 .0x 10-3	*35.8*	7.7	0.047
200.5	1 .0x 10-3	*32.9*	9.7	0.046
199.2	1 .0x 10"3	*39.5*	14.3	0.023
198.4	1.Ox103	*35.2*	16.3	0.022
197.7	1 .0x 10-3	*31.2*	17.2	0.038
197.4	1 .0x 10-3	*30.2*	18.1	0.038
197.4	1 .0x 10-3	*30.2*	18.1	0.035
195.2	1.Ox10-3	15.1	24.2	0.020
220.0		5.0	41.0	0.021[d]
200.0		40.0	10.0	o.045[e]
220.0		5.0	41.0	0.01[f]

[a] Experimental Conditions: $P_{N2O5} \approx 5 \times 10^{-7}$ Torr, $P_{HNO3} \approx 5 \times 10^{-7}$ Torr, $P_{He} = 0.40$ Torr, and flow velocity = 1500 to 1900 cm s-*.

[b] Estimated from the $H_2SO_4/HNO_3/H_2O$ ternary vapor pressure data of Zhang et al. [1993] and Carslaw et al. [1994].

[c] Measurements excluding HNO_3 (average of 4 or more measurements).

[d] Average of 10 experiments performed on a liquid acid solution consisting of 41 wt % HNO_3 and 5 wt % H_2SO_4 at 220 K.

[e] Average of 10 experiments performed on a liquid acid solution consisting of 10 wt % HNO_3 and 40 wt % H_2SO_4 at 200 K.

[f] Average of 5 experiments performed on a partially frozen acid solution consisting of41 wt % HNO_3 and 5 wt % H_2SO_4 at 220 K.

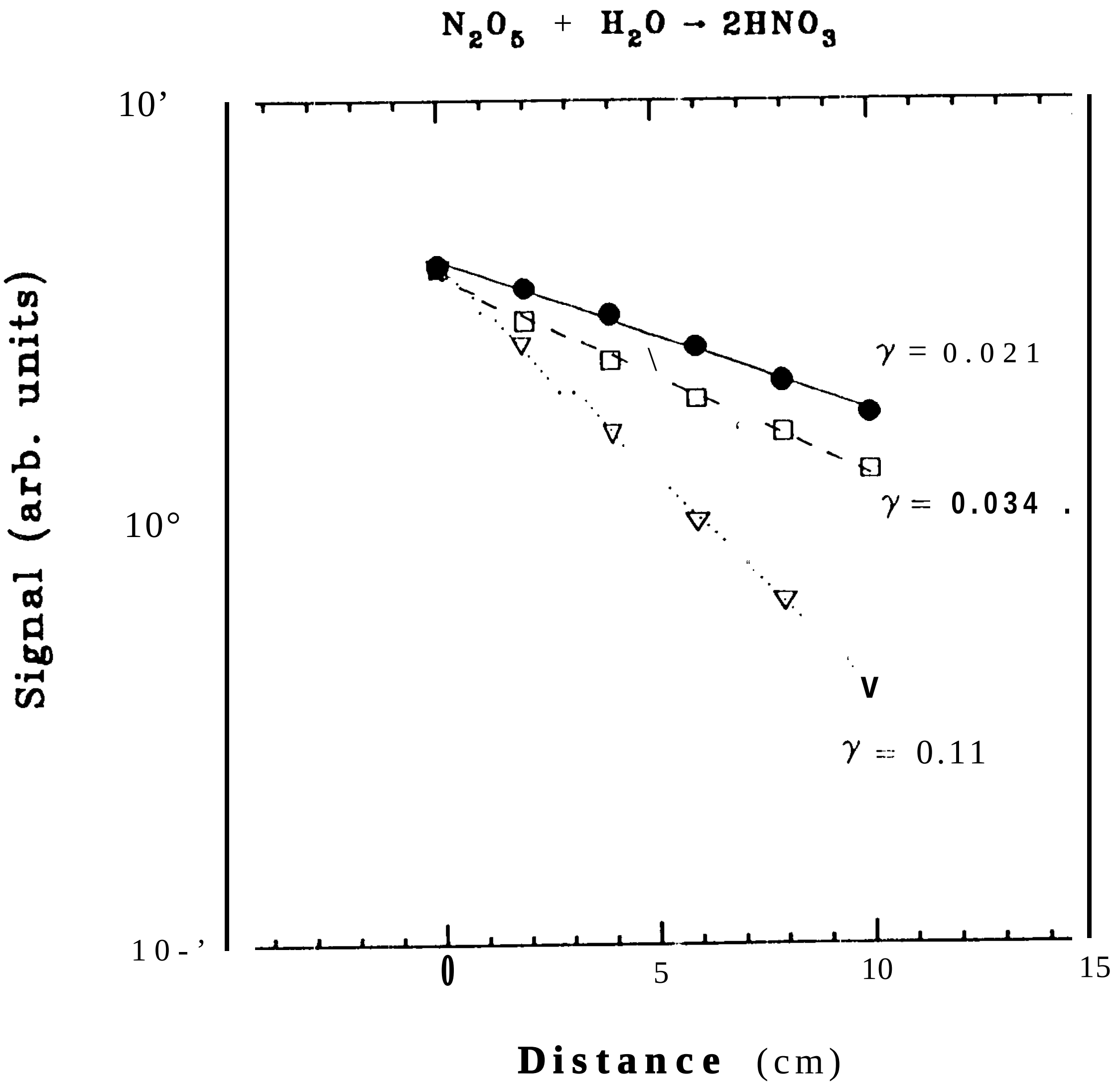
Figure Captions

Figure 1. N_2O_5 signal as a function of injector position as it was exposed to three different acid solutions: (solid circles) 41 wt % HNO_3 and 5 wt % H_2SO_4 at 220 K, (open squares) in the presence of H_2O and HNO_3 at partial pressures of 3.8x 10^{-4} Torr and 5.0x 10^{-7} Torr respective] y at 195 K (corresponding to - 16.4 wt % HNO_3 and 29.4 wt % H_2SO_4), and (open triangles) without HNO_3 at 200 K and P_{H2O} = 3,8x104 Torr (corresponding to - 53 wt % H_2SO_4). The reaction probabilities corresponding to the three cases are 0.021, 0.034, and 0.11, respectively. The lines are least squares fits through the data. Experimental conditions: P_{N2O5} = 5.0x 10^{-7} Torr, P_{He} = 0.40 Torr, and flow velocity = 1500 to 1900 cm s^{-1}.

Figure 2. Reaction probability of N_2O_5 with H_20 as a function of temperature (a) without; (b and c) with HNO_3. The H_2O partial pressure is 3.8x104 Torr in (a) and (c), and 1.0x103 Torr in (b). Each point in (a) is an average of at least four measurements. The lines are least squares fits through the data. Experimental conditions: P_{N2O5} = 5.0x 10^{-7} Torr, P_{He} = 0.40 Torr, P_{HNO3} = 5.0x 10”^{7} Torr, and flow velocity = 1500 to 1900 cm s“’.

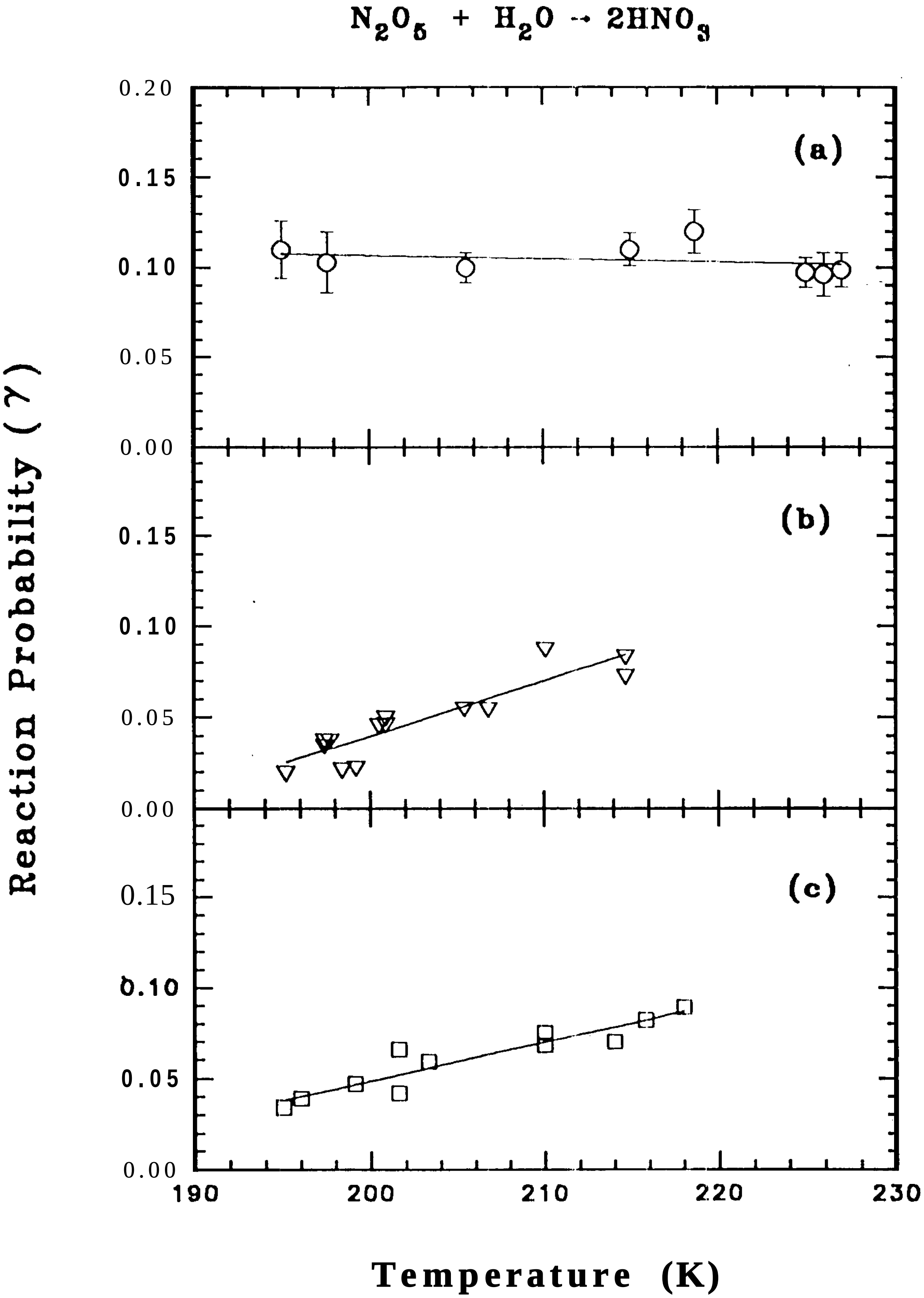
Figure 3. $C10N0_2$ signal as a function of injector position for $ClONO_2$ reaction with H_20 on three different solutions: (solid circles) 41 wt % H NO_3 and 5 wt % H_2SO_4 at 220 K, (open squares) in the presence of H_2O and HNO_3 at partial pressures of 3.8x104 Torr and 5.0x 10-7 Torr respectively at 196 K (corresponding to -9.7 wt %` $HN0_3$ and 37.4 wt % H_2SO_4), and (open triangles) without HNO_3 at 196 K and P_{H2O} = 3.8x104 Torr (corresponding to -48 wt % H_2SO_4). The reaction probabilities corresponding to the three cases are 0.051, 0.039, and 0.041, respectively The partial pressure of $C10N0_2$ used in these experiments was 5.0x 10^{-7} Torr.

Figure 4. Reaction probability of $ClONO_2$ hydrolysis as a function of temperature in the presence of gaseous $HN0_3$ (open circles). Also shown in this figure for comparison is the measurement without HNO_3 (solid curve) under similar conditions [Zhang et al., 1994a]. Experimental conditions: P_{ClONO2} = 5.0x 10-7 Torr, P_{HNO3} = 5.0x 10^{-7} Torr, P_{He} = 0.40 Torr, P_{H2O} = 3.8x10^{-4} Torr, and flow velocity = 1500 to 1900 cm s-’.



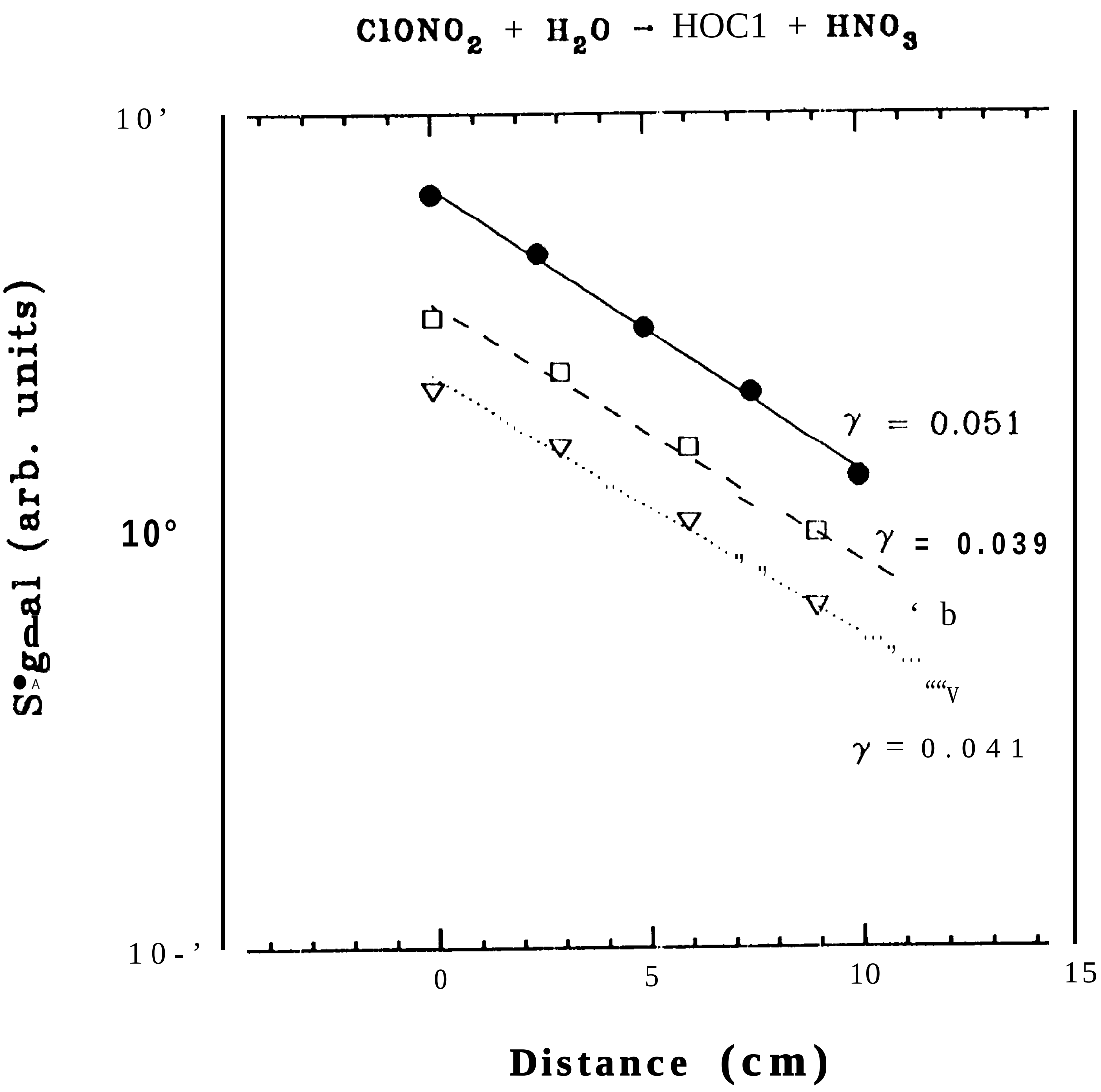
N2O5 + H2O → 2HNO3
10'
10°
10-'
Signal (arb. units)
γ = 0.021
γ = 0.034
γ = 0.11
0
5
10
15
Distance (cm)

Fig. 1



$N_2O_5 + H_2O \rightarrow 2HNO_3$
(a)
(b)
(c)
0.20
0.15
0.10
0.05
0.00
190
200
210
220
230
Reaction Probability (γ)
Temperature (K)

Fig. 2



$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$
10'
10°
10-'
Signal (arb. units)
γ = 0.051
γ = 0.039
γ = 0.041
0
5
10
15
Distance (cm)

Fig. 3

$ClONO_2 + H_2O \rightarrow HOCl + HNO_3$

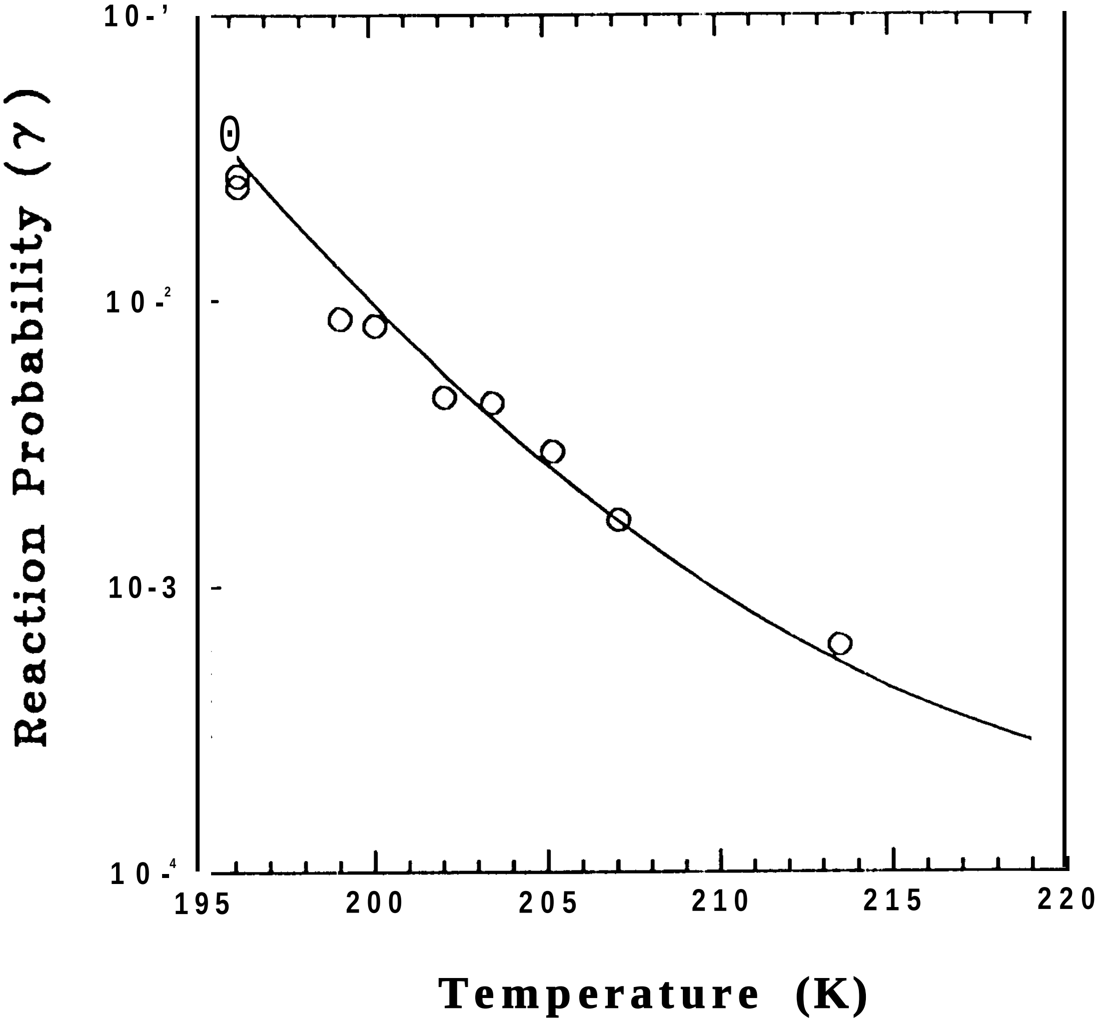


Fig.4